I. THE CONDENSATION OF METHYLMAGNESIUM IODIDE WITH MESITYL KETONES

II. α-MESITYLPROPIONIC ACID

BY

WILLIAM ELDRED WALLACE

B. S., University of Wichita, 1940

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I. THE CONDENSATION OF METHYLMAGNESIUM IODIDE WITH MESITYL KETONES

Introduction

The carbonyl group of mesityl ketones has been known to react additively only with hydrogen. In particular normal or 1,2 addition of a Grignard reagent has never been observed with a simple mesityl ketone.[1] Recently mesityl *t*-butyl diketone was found to undergo 1,2 addition of methylmagnesium iodide to each of the carbonyl groups.[2] Also the conversion of certain mesitoic esters to ketones by the action of Grignard reagents may be explained by assuming 1,2 addition of the reagent to the ester carbonyl group.[3]

These results led to a re-examination of the behavior of mesityl ketones toward the Grignard reagent. The most favorable structure appeared to be that in which the mesitoyl radical was joined to the smallest possible group that possessed no *alpha* hydrogen atom. Among aliphatic radicals *t*-butyl was the logical choice. However, pivalylmesitylene could not be induced to react with methylmagnesium iodide.[2] In the aromatic series certain ketones such as benzoylmesitylene appeared to offer the best chance of realizing 1,2 addition. Studies were made on benzoylmesitylene, *p*-bromobenzoylmesitylene and *p*-toluylmesitylene during this investigation.

Experimental and Discussion

Benzoylmesitylene was treated with methylmagnesium iodide under "forcing" conditions. The expected tertiary carbinol was not isolated but rather the dehydration product, 1-phenyl-1-mesitylethylene, was obtained directly. Similar results were produced when *p*-bromobenzoylmesitylene and *p*-toluylmesitylene were treated with methylmagnesium iodide. In each case the ethylene was a pale yellow oil which could not be crystallized. When 1-phenyl-1-mesitylethylene was treated with 5

per cent ozone three products were isolated. Mesitylphenylacetic acid and β-phenyl-β-mesitylvinyl alcohol were obtained in substantial quantities while mesityl phenyl diketone was isolated in small amount. Only one product, *p*-tolylmesitylacetic acid, was isolated when 1-*p*-tolyl-1-mesitylethylene was ozonized.

Nitration of 1-phenyl-1-mesitylethylene by the procedure of Anschütz and Romig[4] yielded 2-phenyl-2-(3-nitromesityl)-1-nitroethylene. The nitroethylene, which crystallized from ethanol in yellow platelets, exhibited no characteristics of unsaturation toward permanganate solution. Catalytic reduction of 2-phenyl-2-(3-nitromesityl)-1-nitroethylene in the presence of a platinum oxide catalyst converted it to 2-phenyl-2-(3-nitromesityl) vinylamine. This amine, as might be predicted from its vinylogous relationship to an N,N-diarylamine, was completely neutral. The amine hydrochloride could not be formed even in anhydrous ether solution. The acetyl and benzoyl derivatives were readily formed, however. When the vinylamine was treated with dilute hydrochloric acid it was converted to di-[2-phenyl-2-(3-nitromesityl) vinyl] amine. This compound could not be caused to form either a benzoyl or an acetyl derivative. Transformations comparable to the above have been observed by Lipp[5] who employed 2,2-diphenyl-1-nitroethylene.

Treatment of 2-phenyl-2-(3-nitromesityl)-1-nitroethylene, 2-phenyl-2-(3-nitromesityl) vinylamine or di-[2-phenyl-2-(3-nitromesityl) vinyl] amine with stannous chloride and ethanolic hydrochloric acid led to the formation of di-[2-phenyl-2-(3-aminomesityl) vinyl] amine.

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II. α-MESITYLPROPIONIC ACID

Introduction

α-Mesitylpropiomesitylene belongs to that class of ketones whose enol forms are stable.[1] Indeed the synthesis of this substance has been accomplished only by ketonization of 1,2-dimesityl-1-propene-1-ol.[2] A more obvious and presumably more suitable method of synthesis of α-mesitylpropiomesitylene would involve a Friedel-Crafts reaction between α-mesitylpropionyl chloride and mesitylene. Accordingly, attention was centered upon possible synthetic routes to α-mesitylpropionic acid. The present work was undertaken in the hope of finding a convenient synthesis of the acid.

Experimental and Discussion

Treatment of mesitylacetonitrile with ethyl acetate in the presence of sodium ethoxide converted it to α-mesitylacetoacetonitrile. Alkaline hydrolysis of the nitrile formed mesitylacetamide while acid hydrolysis converted it to mesitylacetone. Treatment of α-mesitylacetoacetonitrile with methyl iodide in the presence of sodium ethoxide caused the formation of the O-methyl derivative instead of the expected α-mesityl-α-acetopropionitrile. α-Mesitylacetoacetonitrile could not be converted to ethyl mesitylacetoacetate by treatment with ethanolic hydrogen chloride. Attempts to synthesize ethyl mesitylacetoacetate by treatment of ethyl mesitylacetate with ethyl acetate in the presence of sodium ethoxide were also unsuccessful. Failure likewise attended the attempts to methylate mesitylacetone with methyl iodide in the presence of sodium isopropoxide.

α-Mesitylpropionic acid was finally obtained by hydrolysis of α-mesitylpropionitrile which was formed when mesitylacetonitrile was treated with methyl iodide in the presence of sodium amide. The hydrolysis of α-mesitylpropionitrile was accomplished only with difficulty. Prolonged heating with a mixture of glacial acetic and concentrated sulfuric acids was necessary to effect the conversion. Even after this drastic treatment a considerable amount of neutral product could be isolated

which proved to be α-mesitylpropionamide. This amide was also formed when α-mesitylpropionitrile was heated with alkali and when mesitylpropionyl chloride was treated with concentrated aqueous ammonia.

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Vita

The author was born near Wichita, Kansas, on February 8, 1917. He attended the public schools of that city and was graduated from Wichita High School North in June, 1935. He entered the University of Wichita in September of the same year and was granted the degree of Bachelor of Science in June 1940. In September of that year he entered the Graduate School of the University of Illinois. During the years 1940-1943 he was a teaching assistant in inorganic chemistry.

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